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## MASSIVE TROILITE FROM DEL NORTE COUNTY, CALIFORNIA<sup>1</sup>

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**OCCURRENCE:**—A few specimens of an iron sulfide, supposed to be pyrrhotite because of its bronze brown tarnished surfaces, were brought to me by Mr. Vonsen, who had obtained them from the owner of a copper claim in the northern part of Del Norte County. The specimens showed some properties quite distinct from those for pyrrhotite and the analysis of the mineral proved it to be the monosulfide of iron, FeS. This ferrous sulfide has been observed in nature only as a constituent of meteoric iron and is known as troilite. Its properties have not been determined sufficiently to differentiate it from pyrrhotite, so the Del Norte troilite is an important discovery, not alone on account of its terrestrial origin but also because of its abundance. It agrees with the troilite of the Cañon Diablo meteorite in its properties, pieces of which were kindly given to me by Mr. Merrill, so the two are identical.

**PROPERTIES:**—The Del Norte mineral is distinct from pyrrhotite in several respects. The color is slightly different; it is non-magnetic and it is easily soluble in dilute sulfuric acid. The color of the untarnished mineral is light grayish brown with no bronze tinge. The powder is completely nonmagnetic when tested with a horse-shoe magnet. The magnetism of pyrrhotite varies in intensity, yet it is doubtful if a nonmagnetic variety really exists. It is always classed as a magnetic mineral. From the Del Norte mineral we can infer that the monosulfide is non-magnetic and that pyrrhotite with its excess sulfur is a distinctly different sulfide. In the description of troilite in Dana's System of Mineralogy no

<sup>1</sup> Paper read at the annual meeting of the Mineralogical Society of America, Amherst, Mass., December 29, 1921.

mention is made of its non-magnetic property. The most striking difference between troilite and pyrrhotite lies in their behavior with sulfuric acid. The acid immediately attacks troilite and generates hydrogen sulfide as copiously as it does with the commercial monosulfide of iron used for that purpose. Pyrrhotite remains inert in the acid and a trial of pieces from all the localities represented in our collection showed that not one of them was dissolved by the acid. It requires hydrochloric or nitric acid to dissolve pyrrhotite. This certainly indicates that a sulfide with a formula corresponding to  $Fe_nS_{n+1}$  is chemically and structurally different from one with a formula  $FeS$ .

ANALYSES: The iron could be determined easily by titration of the dilute sulfate solution. Several titrations of each sample were made. For the determination of the sulfur it was necessary to oxidize it by fusion with nitrate and carbonate of potassium or sodium. Nitric acid invariably liberated some sulfur and long boiling in the acid with additions of bromine or potassium chlorate failed to completely oxidize the small globules of free sulfur. The first sample was not carefully separated from its impurities which amounted to seven per cent. The second sample was hand picked and fairly pure.

Analyses:

	I	Ratio	II	Ratio
Fe. ....	58.78%	1.052	62.70	1.123
S. ....	33.62	1.048	35.40	1.104

Both of these samples show a ratio Fe:S practically 1:1.

The mineral is therefore chemically as well as physically the monosulfide of iron,  $FeS$ . The total iron in the samples varied from 64% to 66% but no complete analyses of the inclusions were made, since the portion soluble in sulfuric acid was the troilite. The specific gravity of the second sample was 4.67.

INCLUSIONS:—Small particles and bunches of bluish black serpentine containing much iron occur sparsely disseminated in the massive troilite and it was difficult to completely eliminate them by hand picking. The dilute acid did not dissolve them so they did not affect the analyses of the soluble troilite. A small amount of carbon is also present, making the mineral similar in this respect to the meteoric troilite. A trace of copper, but no nickel or chromium occurs, although chromite was said to occur with the mineral.

The principal inclusion is magnetite. Its brilliant black color separates it distinctly from the troilite. It occurs in granular

patches, some showing minute octahedrons. Some of the rims show a gradation into the troilite and the magnetite appears to be residual patches left from a conversion of a larger mass into troilite.

ORIGIN:—The locality is remote and has not been visited by the writer and the description of the occurrence comes from the owner of the copper claim. He reports that the chalcopyrite bodies occur in a shear zone of serpentine along an extensive fault. This zone consists of fractured, slickensided, and altered rock which has evidently been impregnated by sulfide solutions which deposited the chalcopyrite. The troilite was found in one of the tunnels in rounded masses with smooth, somewhat slickensided surfaces. These were probably magnetite masses in the original serpentine and the solutions carrying hydrogen sulfide transposed them into the sulfide. The large amount of iron appears to have conditioned the formation of the monosulfide instead of the more common pyrrhotite with its excess of sulfur over the iron.

PYRRHOTITE:—Many analyses of pyrrhotite have been made but most of them are of the massive material, since crystals are rare. Doubtless there would be more agreement in the analyses if only pure crystals were analyzed, but as it is the variation is not wide. Sulfur is always in excess of the iron to correspond to a ratio of 1:1, and the analyses yield such formulas as  $Fe_5S_6$ ,  $Fe_7S_8$ ,  $Fe_{11}S_{12}$ , etc. The general formula used to express the composition is  $Fe_nS_{n+1}$ .

The theory of solid solutions of the elements in a mineral has been advanced to explain the variations in the composition of some of our massive minerals and this theory might be extended to pyrrhotite to explain the seeming excess of sulfur. Allen, Crenshaw, Johnston and Larsen<sup>2</sup> in their excellent paper on the mineral sulfides of iron, showed that synthetic pyrrhotite could be formed from pyrite or marcasite which would vary in the ratio of sulfur to iron in the same way as in the natural mineral. From their analyses of the ten synthetic sulfides they calculated that all sulfur in excess of a ratio  $Fe:S=1:1$  was sulfur in solid solution, basing their calculations on the assumption that  $FeS$  was the end member of their pyrrhotite series. Their statement that troilite is nothing more than pyrrhotite and has no right as a separate species or

<sup>2</sup> The Mineral Sulfides of Iron: E. T. Allen, J. L. Crenshaw and J. Johnston with crystallographic study by E. S. Larsen. *Amer. Jour. Sci.*, **33**, 169-236, 1912.

name since it is only the end member of the series, does not conform to the facts. Troilite and pyrrhotite are too distinct in their properties to be considered in the same series. In some of our later textbooks the formula for pyrrhotite is stated as  $\text{FeS}$ . No analysis of pyrrhotite shows this to be the case; on the contrary all of the analyses conform to the generally accepted formula  $\text{Fe}_n\text{S}_{n+1}$ . The formula  $\text{Fe}_{11}\text{S}_{12}$ , which approximately agrees with the composition of most pyrrhotites, if considered as  $\text{FeS}+\text{S}$  in solid solution, contains 3.22% excess sulfur. It seems quite improbable that this small excess held as solid solution would convert non-magnetic, easily soluble troilite into magnetic, insoluble pyrrhotite. The magnetic property and general composition of pyrrhotite certainly indicate a chemical difference from the other iron sulfides and in fact, suggest an analogy to magnetite. The ferrous and ferric oxides alone are non-magnetic but in combination form a strongly magnetic compound. Pyrrhotite is considered wholly a ferrous sulfide while its magnetism suggests the presence of the ferric molecule and a formula such as  $\text{Fe}_3\text{S}_4$  would still conform to the general formula  $\text{Fe}_n\text{S}_{n+1}$ . Carrying out this idea which is offered merely as a suggestion,  $\text{Fe}_3\text{S}_4$  might be considered as an end member for pyrrhotite and variations in composition be ascribed to excess percentages of the ferrous sulfide, perhaps present as solid solution.

### CERULEOFIBRITE, A NEW MINERAL<sup>1</sup>

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Several specimens of cuprite, in the Mineralogical Museum of the University of Michigan, contained a blue, fibrous mineral which has proven to be a new species. The proposed name, ceruleofibrite, is from the Latin *caeruleus*, blue, and *fibra*, a fiber.

These specimens were purchased from the Foote Mineral Company, and were labelled from "Bisbee, Arizona." They are composed chiefly of cuprite, containing disseminated flakes of copper, associated with azurite, chrysocolla, and small crystals of brochantite. Another specimen, obtained from Ward's Natural Science Establishment which was in reality ceruleofibrite, was labelled "conellite on cuprite," the locality being given as Lowell, which is in the Bisbee district.

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